

# MIXTURES OF GASES

THOMAS A. KNOTTS IV

## 1. EQUATIONS OF STATE FOR MIXTURES OF GASES: ALL EOS'S BUT VIRIAL

The PVT behavior of a pure-component gas can be modeled using an equation of state (EOS) such as virial, Soave-Redlich-Kwong or Peng-Robinson. Each of these equations have certain constants which are based upon pure-component properties such as acentric factor and critical constants. So how do you determine the PVT behavior of a *mixture* of gases? You essentially need equation of state constants for the **mixture** rather than the pure component. These mixture constants can be obtained using so-called **mixing rules**. For all but the virial equation of state, the mixing rules are empirical and have little theoretical basis. Their utility is based solely upon their ability to reproduce experimental behavior. As such, several versions of mixing rules have been proposed. For the present purposes, the following forms may be used. These are termed the van der Waals mixing rules.

$$\begin{aligned}a &= \sum_i \sum_j y_i y_j a_{ij} \\ a\alpha &= \sum_i \sum_j y_i y_j (a\alpha)_{ij} \\ b &= \sum_i y_i b_i\end{aligned}$$

In each of the equations above,  $a$  is the *mixture* value and  $a_i$  is the value for *pure component*  $i$ . This is the same for  $b$  and  $b_i$ , and  $\alpha$  and  $\alpha_i$ . The mixing rules for  $a$  and  $\alpha$  contain the interaction parameters  $a_{ij}$  and  $\alpha_{ij}$ . These are evaluated using the **combining rules** found below.

$$\begin{aligned}a_{ij} &= \sqrt{a_i a_j} \\ (a\alpha)_{ij} &= \sqrt{(a\alpha)_i (a\alpha)_j}\end{aligned}$$

These combining rules are sufficient for mixtures of simple or chemically similar compounds. For more complex mixtures, the following combining rule may be used.

$$(a\alpha)_{ij} = (1 - k_{ij}) \sqrt{(a\alpha)_i (a\alpha)_j}$$

In this equation,  $k_{ij}$  is the *binary interaction parameter* with  $k_{ij} = k_{ji}$  and  $k_{ii} = k_{jj} = 0$ . These parameters are found from experiment for every  $ij$  pair and are usually used in conjunction with 3-parameter (or more) equations of state such as Soave-Redlich-Kwong and Peng-Robinson. In practice, if  $k_{ij}$  is not known, it is set equal to zero.

The advantage of using the mixing and combining rules shown above is that the mixture properties can be calculated using only the pure component properties. However, this simplicity means that the equations begin to fail for complex systems. In such cases, more advanced rules are needed and can be found in the literature.

## 2. THE VIRIAL EOS (AND CORRESPONDING STATES) FOR MIXTURES OF GASES

From statistical mechanics, the second virial coefficient of a mixture can be calculated by

$$(2.1) \quad B = \sum_i \sum_j y_i y_j B_{ij}$$

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where  $B_{ii}$  and  $B_{jj}$  are the pure component virial coefficient of species  $i$  and  $j$  respectively. The only question that remains is how to calculate the *cross* coefficient,  $B_{ij}$ . For this, we use corresponding states for the mixture. The following rules are applicable.

$$(2.2) \quad \omega_{ij} = \frac{\omega_i + \omega_j}{2}$$

$$(2.3) \quad T_{c_{ij}} = (T_{c_i} T_{c_j})^{1/2} (1 - k_{ij})$$

$$(2.4) \quad P_{c_{ij}} = \frac{Z_{c_{ij}} R T_{c_{ij}}}{V_{c_{ij}}}$$

$$(2.5) \quad Z_{c_{ij}} = \frac{Z_{c_i} + Z_{c_j}}{2}$$

$$(2.6) \quad V_{c_{ij}} = \left( \frac{V_{c_i}^{1/3} + V_{c_j}^{1/3}}{2} \right)^3$$

These equations can be used to calculate the cross virial coefficient using the Pitzer equations.